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SEPARATION OF MINERAL OIL IN WATER EMULSIONS BY ELECTROCOAGULATION

Abstract

The influence of the applied electrical current and time of electrocoagulation on efficiency of the separation process of a mineral oil in water emulsion was investigated by measuring the total organic carbon, volume of filtrate, mass of separated oil phase, as well ass the aluminum electrodes consumption. Results demonstrated a high efficiency of hydrocarbons' removal form water emulsion, more than 96%, expressed relative to the total organic carbon in water and for all applied currents. Water effluent was clear, without color and odor. The current efficiency increases with the increasing solution electrical conductivity and decreasing current density. Electrocoagulation has shown as a very fast method; time required for a complete separation of emulsion was 50 min for the current of 0.1 A and less than 10 min for the current of 1.0 A.

Introduction

The oil in water emulsions are widely used in metalworking since they include very useful properties of cooling and surface cleaning, protection against the corrosion as well as lubrication [1-3]. Because of the high working temperature, mechanical strain and microorganism present in the environment, emulsions cease to meet the requirements with time and they should be adequately cared for. This should be in agreement with the environmental legislative since the waste emulsions are toxic due to the high content of hydrocarbons, metals and other compounds, such as emulsifiers and other surface active agents, biocides and corrosion inhibitors.

In this work, the recovery of mineral oil in oil-in-water emulsion by separation of water and oil phase applying electrochemical coagulation, i.e. electrocoagulation (EC), is described. There is no need for addition of metal salts or polymers which are usually used for the separation of stable emulsions and oil absorption, removal of metals, colloid particles or soluble inorganic pollutants since the coagulant is formed *in situ* by electrochemical oxidation of anode [4,5].

Experimental

Process

Electrocoagulation processes were performed in bulk, in a glass reactor with the aluminium electrodes (anode and cathode). Scheme of the apparatus and electrical circuit for electrocoagulation is shown in Figure 1. The surface of anode was equal to that of cathode and amounted 12 cm^2. The mixing rate was constant at 240 rpm. The initial values of pH, electrical conductivity and total organic carbon (TOC) of emulsion were determined. The influence of current and time on the separation of emulsion were investigated, whereas the electrocoagulation effectiveness and current efficiency were examined by measuring the loss of the electrodes mass, precipitate mass, voltage between electrodes, volume and the total organic carbon of filtrate.

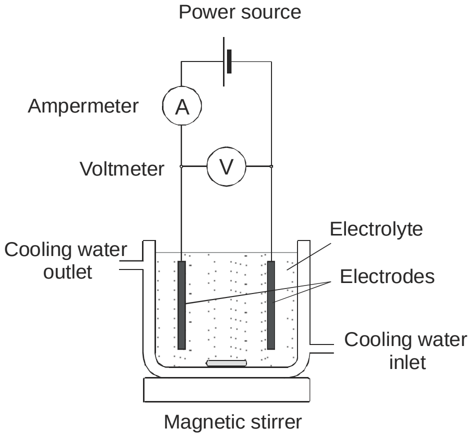
Methods

Apparatus Handylab pH / LF 12 was used for the measurements of pH and electrical conductivity (κ) of solutions. Conductometer was calibrated using KCl solution. The total organic carbon of samples was measured using the Total Organic Analyzer, Shimadzu.

Materials

The deionized water and INA BU-7 concentrate (Maziva Zagreb, d.o.o.), containing mineral oil and additives. For the preparation of emulsion emulsifier, coemulsifier, corrosion inhibitor, flocculants and biocides, were used. The final amount of the oil in emulsion was 1.2 wt. %, where the total organic carbon value was 14520 mg l^{-1}.

Figure 1: Schematic diagram of the apparatus and electrical circuit for electrocoagulation



Results and discussion

Electrical conductivity of electrolytes

The energy consumption in an electrocoagulation process can be expressed with the following equation:

$$E_c = E_c^r + \Sigma\ |\eta|\ + \Sigma\ I\ R \qquad (1)$$

where E_c^r is the value of equilibrium cell potential (V), $\Sigma\ |\eta|$ the sum of absolute values of electrodes' overpotentials (V) and $\Sigma\ IR$ the sum of ohmic drops of potentials in the system (V). In order to reduce the energy consumption it is necessary to reduce the total voltage of the cell, E_c, by reducing the contribution of each equation member. Since the electrolyte, reactor geometry and material of electrodes were predetermined, which further considers the mechanism and kinetics of reactions, and therefore not closer examined, this correlation counts for:

$$E_\Omega = I\ R = I \times (1 / \kappa) \times (\ell / S) = = I \times (const. / \kappa) \qquad (2)$$

where I presents the current (A), R the electrical resistance (Ω), ℓ the distance (m), S the surface area (m^2) and κ the electrical conductivity ($S\ m^{-1}$). Electrical conductivity of the emulsion was relatively low due to the use of deionized water and amounted 0.47 $mS\ cm^{-1}$. The emulsion conductivity increases with addition of soluble salt, NaCl, whereas interdependence of the electrical conductivity and pH of emulsion on the concentration of added salt is shown in Figure 2. The pH does not change significantly as a result of added NaCl, $\Delta pH = 0.35$, unlike conductivity that increases significantly with increasing amount of added salt, within the observed concentrations range. For the salt shares higher than 1 wt. % the emulsion ceases to be stable, therefore the share of 0.8 wt. % was selected for further electrocoagulation experiments. In that way, a satisfying conductivity increase resulted, the emulsion stability was maintained, whereas a relatively low amount of salt was added. Chloride ions resulting from the salt dissociation contribute to the aluminium anode corrosion, to the small extent, and moreover hinder the formation of a passive oxide layer on the electrodes, thus reducing the overpotentials for the anode reaction of aluminium dissolution, as well as the cathodic reaction of hydrogen development [6,7]. These activities are not pronounced and are in favor of the electrocoagulation process [8].

Reactions at the electrodes

Electrolytical dissolution of aluminium anode leads to the formation of monomeric cations, such as Al^{3+} and $Al(OH)_2^+$ at low pH. With pH increase these species hydrolyze further to $Al(OH)_3$ and polymerize finally to $Al_n(OH)_{3n}$ according to the reactions [9]:

$$Al \rightarrow Al^{3+}_{(aq)} + 3\ e^- \qquad (3)$$

$$Al^{3+}_{(aq)} + 3\ H_2O \rightarrow Al(OH)_3 + 3\ H^+_{(aq)} \quad (4)$$

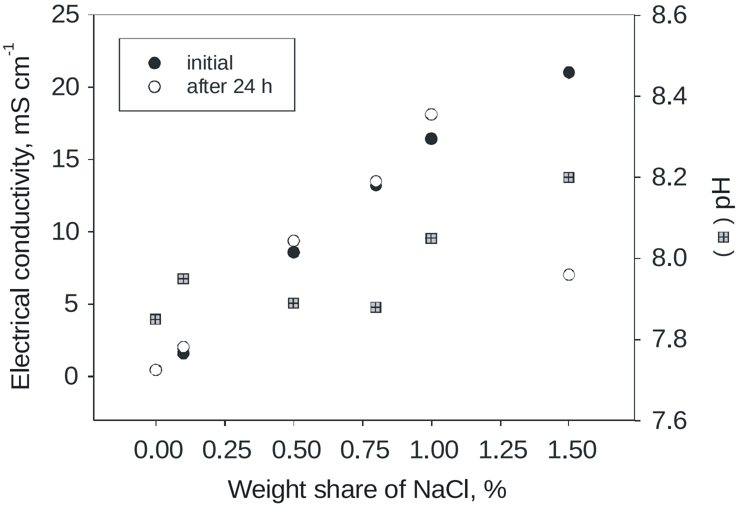
$$n\ Al(OH)_3 \rightarrow Al_n(OH)_{3n} \quad (5)$$

Depending on the pH of water medium the variety of ionic species can be generated, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ or $Al(OH)_4^-$, respectively, the various forms of charged Al^{3+} polyhydroxydes are present [10]. Such charged gel hydroxy complexes are very effective coagulants. Simultaneously with anode dissolution, the water electrolysis takes place at the electrodes; to the smaller extent, depending on the voltage applied, at the anode, while the hydrogen evolution is prevailing reaction at the cathode [4]. The hydrogen evolution, in a neutral and alkaline medium, takes place according to the following reaction [11]:

$$2\ H_2O_{(l)} + 2\ e^- \rightarrow H_{2\ (g)} + 2\ OH^-_{(aq)} \quad (6)$$

During the EC process at electrodes bubbles of oxygen evolve at the anode and, especially, hydrogen at the cathode. Thereby, simultaneously with electrocoagulation, the electroflotation takes places which contributes to the more effective separation and removal of impurities from the solution bulk [4,9]. The multitude of different electrochemical, as well as chemical reactions is possible at the electrodes [4,5,8-10].

Figure 2: The electrical conductivity and pH of electrolyte depending on the weight of added NaCl



The mass of metal that dissolves or precipitates during reaction at the electrode is defined by Faraday's low:

$$Q = I\,t = z\,n\,F = z\,m\,F\,/\,M \tag{7}$$

where Q presents the electrical charge (C), I the current (A), t the time (s), z the number of electrons, n the number of moles of electrons, m the mass (g), M the relative molar mass of the electrode concerned (g mol^{-1}) while F the Faraday's constant (96485 C mol^{-1}).

Process

The electrocoagulation process of studied mineral oil in water emulsion was investigated for three different currents: 0.1 A, 0.5 A and 1.0 A. Table 1 presents the theoretical and experimental changes of the anode mass, cell potential (voltage between the anode and cathode), volume of filtrate, mass of dried precipitate and the total organic carbon of solution depending on the operating current that was kept constant, and the running time.

Cell potential. The interdependence between the current and voltage between the electrodes can be described by *Ohm* law: the initial and final voltages increase linearly with the current increase whereas the values of resistance are 9.54 and 7.85 Ω (the coefficients of regression amount 0.967 and 0.993). At the constant current, voltage decreases slightly with time and reaches constant values. The cause for the voltage reduction is the splitting up of emulsion. Separation of the oil phase leads to the increase of conductivity in the system. Accordingly, the electrocoagulation progress can easily be followed, but only apparently because the potential is mostly not a sufficient or unambiguous parameter.

Current efficiency and the anode electrode wear. With regard to the anode dissolution, it is desirable that its mass change is as close as possible to the theoretical one; in that case the electric current is consumed, to the greatest extent for the formation of aluminum cations whereas current efficiency approaches the value of 100 %. According to the data given in Table 1, one can see that for the current of 0.1 A there is a good agreement between the theoretical and experimental values of the mass change. Oppositely, in case of stronger currents this mass change is significantly lower than the theoretically calculated. These observations are in line with the thermodynamic and kinetic principles in electrochemistry [12,13]. As the current increases, the reaction rate at the electrode increases, as well. But with alienation from the equilibrium stage the yield of charge of the reaction decreases, simultaneously. Thus, current efficiency for the anodic reaction of aluminium dissolution is 100 % for the current power of 0.1 A, 44 % for 0.5 A and 38 % for 1 A. It is significant that the efficiency decreases vehemently with current increase from 0.1 to 0.5 A, where the recorded correlation enables process modeling towards given kinetics and/or efficiency.

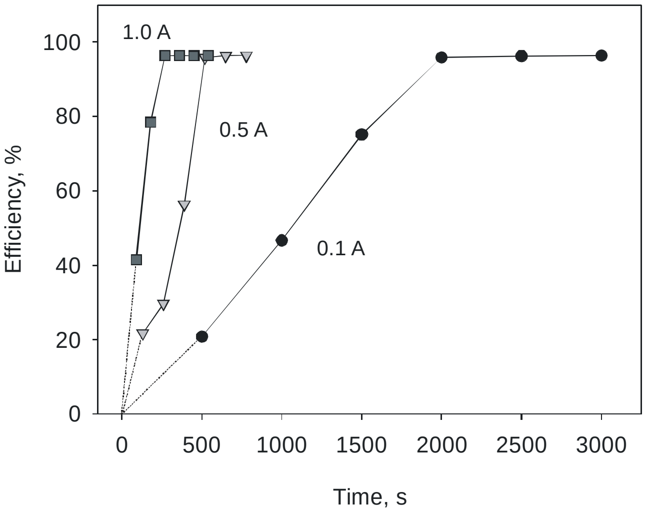
Volume of filtrate and the mass of precipitate. After finishing every bulk experiment, incurred precipitate was removed by filtration, whereas the lag water was removed by drying and the mass was measured. Moreover, volume of the filtrate was measured correlated with the time and these values, depending on the operating current are presented in Table 1. Mass of the dry precipitate increases with increasing duration of the process, where an abrupt increase of the precipitate's mass was observed in the second half of the process, for all the operating currents. A discernible precipitation takes place and more complete removal thereby. Accordingly, volume of the filtrate decreases with increasing duration of the process. Both quantities are of comparable sizes, concerning reached final values, in case of all three operating currents. Small differences that occurred are the consequence of experimental conditions; a relatively low amount of emulsion, difference in the kinetics of nucleation process, coagulation, precipitation and flotation, particle size distribution, etc.

Table 1: Theoretical ($\Delta m_{a/teor}$) and experimental ($\Delta m_{a/exp}$) change of the mass of anode, the mass of precipitate, cell potential (E_c), volume of filtrate ($V_{filtrate}$) and the total organic carbon (TOC) of solution depending on the applied current and time of the electrocoagulation

I, A	t, s	E_c, V	$\Delta m_{a/exp}$, mg	$\Delta m_{a/teor}$, mg	$m_{precipitate}$, g	$V_{filtrate}$, mL	TOC, mg L^{-1}
0.1	500	2.02	0.002	0.005	0.113	-	11500
	1000	1.96	0.003	0.009	0.125	-	7751
	1500	1.88	0.014	0.014	0.631	70.0	3607
	2000	1.87	0.017	0.017	1.175	68.0	602.0
	2500	1.81	0.029	0.026	1.354	66.5	551.4
	3000	1.81	0.030	0.028	1.413	64.5	530.1
0.5	130	7.26	0.004	0.006	0.094	-	11370
	260	6.91	0.004	0.012	0.158	-	10210
	390	5.98	0.007	0.018	0.640	70.0	6340
	520	5.67	0.009	0.024	1.250	66.5	606.7
	650	5.67	0.014	0.030	1.171	65.0	531.0
	780	5.49	0.016	0.036	1.279	58.0	527.1
1.0	90	10.71	0.003	0.008	0.109	-	8500
	180	9.84	0.004	0.017	0.446	-	3138
	270	9.32	0.005	0.025	1.245	66.5	536.7
	360	8.45	0.012	0.034	1.302	64.5	528.1
	450	8.70	0.015	0.042	1.392	63.0	539.5
	540	8.91	0.019	0.050	1.300	61.0	529.9

Total organic carbon. Effectiveness of the electrocoagulation process for splitting of the mineral oil in water emulsions is sized by measuring the total organic carbon in water phase obtained by filtration after the process completion. The values are given in Table 1. The total organic carbon decreases from the initial value of 14520 mg l^{-1} to around 530 mg l^{-1}, for all three currents applied. Calculated efficiency of the process is 96.5 ± 0.2 %, expressed with the total organic carbon (mineral oil and organic additives) removed from the water phase. Figure 3 shows the efficiency of electrocoagulation depending on the time and operating current of the process. With increasing current the time required for the process completion decreases, but also the current efficiency of aluminum dissolution at the anode. Since the effectiveness of process does not change significantly with the current variation, the process rate, as well as energy consumption can easily be controlled; in a very fast process of 540 s with the current of 1 A, around 1.5 Wh of energy is consumed and the current efficiency is around 40 %, while in a slow process of 3000 s with the current of 0.1 A the current efficiency is 100 % and consumed energy is around 0.15 Wh.

Figure 3: Effectiveness of the electrocoagulation process for removal of the total organic carbon from the mineral oil in water emulsion depending on the time and operating current; TOC_o – total organic carbon at the beginning of process, TOC_z – total organic carbon after the completion of process



Conclusion

Electrocoagulation is a complex process that involves several physical, chemical and electrochemical steps. However, it is simple to perform and can be applied for many diverse systems. In this investigation, electrocoagulation is used for simple breaking of the mineral oil in water emulsion where removal of 96 % of the initially present organic carbon was achieved, for all examined process conditions. Efficiency of the process can be increased additionally by enlargement of the working surface of electrodes, cell geometry and regime of mixing, according to the well known chemical and engineering rules. In addition, water treated by electrocoagulation has significantly lower organic content and, therefore, can easily be treated further with other methods. The persistence of its output characteristics, i.e. total organic carbon, presents an advantage of this procedure compared to the methods with a notable deviation of their output characteristics.

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541.18.045	emulzije, odjeljivanje elektrokoagulacijom	emulsion, separation by elektocoagulation

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